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Laboratory Experiment

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Electroless Deposition on Three Substrates: Brass Washers, Cicada Exoskeletons, and Beetles

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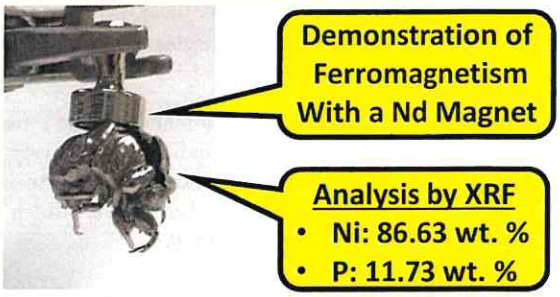
Supporting Information

ABSTRACT: This laboratory experiment showcases electroless deposition, an autocatalytic reduction process performed in aqueous solution containing a metal ion in the presence of a reducing agent yielding a coherent metal film. One set of experiments has been performed by second-semester general chemistry students in a 3 h lab session. After preparing an electroless nickel plating bath, they first plate a brass washer with nickel for 10 min at 85 °C. Using weight gain data for their brass washer along with its surface area, the thickness of the nickel coating is determined. The same electroless nickel plating bath is then used to plate a pretreated cicada exoskeleton with nickel. The three-step pretreatment procedure deposits Pd(s) nanoparticles on a nonconducting exoskeleton made of chitin, transforming it into a conducting substrate. A second set of experiments has been performed by upper-class chemistry majors. They (1) explore the reproducibility in weight gain when plating brass washers with nickel for 10, 20, 30, and 40 min time intervals, (2) plate beetles with nickel, and (3) plate cicada exoskeletons with copper using an electroless copper plating bath recipe they find in the literature. Weight gain data and photos of the plated cicada exoskeletons and beetles accompany this article. The nickel-plated brass washers and cicada exoskeletons were examined with XRF spectrometry. This analysis demonstrates that the nickel coating is not pure nickel but rather an alloy containing phosphorus.



KEYWORDS: *First-Year Undergraduate/General, Upper-Division Undergraduate, Laboratory Instruction, Hands-On Learning/Manipulatives, Electrochemistry, Industrial Chemistry, Materials Science, Metals, Oxidation/Reduction*

INTRODUCTION

This experiment describes the process of depositing a nickel coating by electroless deposition on the surfaces of three different substrates: brass washers, cicada exoskeletons, and beetles. Electroless copper deposition on cicada exoskeletons is also described. Weight gain data for the brass washers and photos of the cicada exoskeletons and beetles accompany this article. In addition, the resulting nickel coatings deposited on the brass washers and cicada exoskeletons were examined by X-ray fluorescence (XRF) spectrometry.

Two different student populations have performed portions of these experiments. Undergraduate engineering students in a second-semester general chemistry course have performed this experiment in one 3 h lab period. These students plated brass washers and cicada exoskeletons with nickel. The timing of the experiment was designed to coincide with the treatment of electrochemistry in the lecture portion of the course.

Chemistry majors in an advanced inorganic lab course have also performed electroless deposition experiments. These include (1) a study of the reproducibility of the weight gain in brass washers plated by electroless nickel deposition for different plating times, (2) electroless nickel deposition on beetles, and (3) electroless copper deposition on cicada exoskeletons.

We have also developed a lab experiment that illustrates electroless deposition on plastic objects made of ABS. This experiment will be described in a separate article, because it requires etching the ABS surface, but etching is not required for the substrates described here.

The topic of electroless deposition has received scant treatment in this *Journal*. Krulik, in a review article[1] that appeared in this *Journal* in 1978, defined electroless deposition as "the controlled autocatalytic reduction of a dissolved metal ion by a dissolved reducing agent at an interface to give a uniform, coherent film". Two very brief lab experiments illustrating electroless copper deposition also appeared in this *Journal* in the late 1970s. One described the process of electroplating polyethylene with copper, which necessitated electroless deposition of copper prior to the electroplating process.[2] A second article described the procedure required for making a copper mirror by electroless deposition on treated glass.[3]

This experiment also represents an ongoing effort by one of us (C.J.D.) to develop lab experiments that showcase applied

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Table 1. Comparison of Plating Techniques

Technique	Source of Electrons	Anode	Cathode	Substrate
Immersion plating	Substrate (it is the reducing agent)	None	None	Oxidized while being plated
Electroplating	Outside energy source (i.e., power supply)	Source of metal ions or inert electrode	Substrate to be plated	Not oxidized, just plated
Electroless deposition	Dissolved reducing agent in the plating bath	None	None	Not oxidized, just plated

Table 2. Categories of Substrates Based on the Pretreatment Protocol Required Prior to Electroless Deposition

Category	Substrate	Comment
1	Active metals (e.g., Ni, Co, Fe, Al, and Zn)	No pretreatment is required (the process is spontaneous).
2	Less active metals (Cu and Cu alloys, e.g., bronze and brass)	Galvanic initiation by a metal from Category 1 is required.
3	Metals that are catalytic poisons (e.g., Pb, Cd, Sb, and Bi)	Electroplated active metal coating (e.g., Ni) is needed prior to the electroless deposition process.
4	Polar nonconducting substrates (e.g., cicada exoskeletons)	Prior deposition of Pd(s) or other metal on the surface of the substrate is required.
5	Nonpolar nonconducting substrates (e.g., objects made of ABS and PET)	Prior etching of the substrate (in order to create polar surface functional groups) followed by deposition of Pd(s) or other metal on the surface of the substrate is required.

chemistry.[4−10] These lab experiments support a two-semester general chemistry sequence populated exclusively by undergraduate engineering students that employs the overarching theme of *Chemistry and the Automobile*, which has been previously described in this *Journal*.[4]

BACKGROUND

Electroless deposition has been an important industrial process for over 50 years, following its accidental discovery by A. Brenner and G. Riddel in 1944.[1] It remains a process that continues to be investigated and refined, and its applications continue to be expanded. A recent search of the entire suite of ACS journals using the following phrases yielded hundreds of hits (the exact numbers are provided in parentheses): electroless deposition (2143), electroless copper (1061), electroless nickel (670), electroless gold (1282), electroless silver (1028), and electroless cobalt (281).[11]

There are many reasons why electroless deposition is performed,[12] including the following:

- To create a decorative or lustrous surface.
- To increase the corrosion resistance of a substrate.
- To harden a surface and increase wear resistance.
- To modify the conductivity of a surface (often this involves electroless deposition of a metallic coating on a nonconducting surface that is subsequently electroplated).
- To improve the lubricity of a surface.
- To provide a highly solderable surface.
- To achieve a metallic coating with superior uniform thickness (a goal that cannot be achieved by electroplating).

Table 1 compares and contrasts three plating techniques: immersion plating, electroplating, and electroless deposition. The latter two methods are extensively employed in industry. Immersion plating, a process in which a less noble (or more active) metal (e.g., Zn) is immersed in a solution containing more noble metal ions (e.g., Cu^{2+}), is not a practical method for depositing a metal coating on a substrate because, among other reasons, the coating does not adhere tightly to the substrate. Immersion plating and electroless plating are alike in that they do not require an outside source of electrons; that is, there is no anode or cathode as part of the setup required for electroplating. They differ in that electroless deposition is an autocatalytic process, whereas immersion plating is not.

Given the proper pretreatment protocol, electroless deposition can be performed on a wide range of substrates, including both conducting and nonconducting substrates. In Table 2, substrates suitable for electroless deposition are subdivided into five categories on the basis of the nature of the pretreatment protocol required (if any) to modify the surface of the substrate prior to electroless deposition.[13]

The three substrates employed in this lab experiment, brass washers, cicada exoskeletons, and beetles, fall in Categories 2 (brass washer) and 4 (cicada exoskeleton and beetle). Plating on plastic (e.g., ABS) falls in Category 5.

ELECTROLESS NICKEL DEPOSITION

Several review articles[12,14,15] and books[16−18] addressing electroless nickel deposition have recently appeared. Sahoo and Das[12] identify two types of mechanisms for electroless nickel deposition using hypophosphite as the reducing agent: (1) an *electrochemical mechanism* and (2) an *atomic hydrogen mechanism*. They add that the deposition reactions are still not well understood. The details of these mechanisms are provided in the Supporting Information (Section S1).

Table 3. Role of the Chemicals Present in an Electroless Nickel Plating Bath

Compound	Function
Ni(II) cation (e.g., nickel(II) sulfate heptahydrate)	Source of metal to be deposited on substrate
Reducing agent (e.g., sodium hypophosphite)	Source of electrons for the reduction processes
Complexing agents (e.g., acetate and citrate)	Stabilization of the plating bath solution
Accelerators	Activation of the reducing agent
Buffers	Stabilization of the pH of the plating bath
Stabilizers (e.g., thiourea and Pb(II))	Prevention of plating bath decomposition
Wetting agents (e.g., ionic and nonionic surfactants)	Improvement of the wettability of the substrate surface

Both mechanisms account for several experimentally observed outcomes: (1) the reduction of Ni^{2+} to Ni(s), (2) the evolution of hydrogen gas during the electroless nickel

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plating process, and (3) the incorporation of elemental phosphorus in the Ni coating. The P content in the Ni coating is affected by several variables, such as the pH of the plating bath and the concentrations of both the Ni^{2+} ion and the hypophosphite ion in the bathing bath.[19]

Table 3 summarizes the composition of a typical electroless nickel plating bath along with the roles the chemicals perform.[14] Recipes for electroless nickel baths abound.[17] Commercial formulations are also available.

The aqueous solution containing the Ni(II) ion and the reducing agent has been described as a "metastable equilibrium".[13] Thus, one of the only disadvantages associated with electroless deposition is the limited lifetime of the plating bath. In extreme cases where the ratio of chemical components is out of balance, the bath will *crash*. Crashing is often accompanied by the following events: rapid evolution of $H_2(g)$, deposition of Ni(s) on all the surfaces the plating bath is in contact with, and precipitation of nickel phosphite. To achieve bath stability, the Ni content of the plating bath is formulated to be low (0.007 to 0.03 M). In addition, complexing agents, accelerators, buffers, and stabilizers are added to the plating bath to enhance bath stability. Complexing agents fulfill several roles, including the retardation of nickel(II) phosphite precipitation.[15] Buffers are employed in the plating bath because H^+ ions are generated during the electroless plating process.

The temperature of the plating bath is also an important factor. Most nickel electroless plating baths are used at 75 ± 15 °C. The deposition rate increases exponentially with increased temperature (all other factors being equal). The likelihood of bath "plate-out" (or crashing) increases when the plating bath temperature is very high (>90 °C).[17]

Although immersion plating and electroplating yield coatings consisting of a pure metal, electroless nickel deposition yields a nickel alloy containing Ni(s) plus a nonmetal atom (e.g., B or P). The presence of the B or P atoms in the nickel alloy originates from the reducing agent. The P atoms come from the hypophosphite anion ($H_2PO_2^-$), the most commonly used reducing agent, and the B atoms originate from either borohydride (BH_4^-) or dimethylamineborane ($(CH_3)_2NH{\cdot}BH_3$), alternative reducing agents.[14]

ELECTROLESS COPPER DEPOSITION

The main aqueous redox reaction for the electroless copper plating process is provided below (see reaction 1).[20]

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu(s) + 2HCOO^- + 2H_2O + H_2(g) \quad (1)$$

The pH of electroless copper plating bath is adjusted to ~12.5 by the addition of sodium hydroxide, and the bath is operated at temperatures ranging from room temperature to 60 °C. Most formulations of electroless copper plating baths rely on one of two reducing agents: formaldehyde (HCHO) or glyoxylic acid ($HCOCO_2H$). Formaldehyde has been the traditional reducing agent of choice, whereas glyoxylic acid has been introduced as a less toxic alternative to formaldehyde. The standard reduction potentials for these two reducing agents are very similar.[21] Additional information pertaining to the composition of a copper electroless plating bath is provided in the Supporting Information (Section S2).

CHOICE OF SUBSTRATES

Brass washers were selected as a substrate for nickel electroless deposition for several reasons:

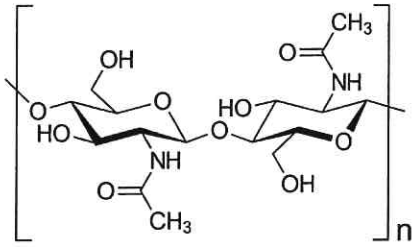

Figure 1. Structure of chitin with two *N*-acetylglucosamine repeat units. Public domain image reproduced from Wikimedia Commons.[22]

- They are inexpensive.
- The color change they undergo during electroless deposition visually illustrates that nickel has been deposited on the surface of the washer.
- Their shape allows for a convenient way to suspend them in the plating bath (see below).
- They are a logical choice for a Category 2 substrate (see Table 2).

Most nonconducting substrates have to be etched (e.g., with chromic acid) as part of the pretreatment protocol before they can be plated by electroless deposition. Etching creates polar functional groups (e.g., hydroxyl, carboxyl, and sulfate groups), which are necessary to chelate the Sn(II) cations (see below). Etching also transforms a hydrophobic surface into one that is more hydrophilic, which is desirable because plating takes place in aqueous solution.

The cicada exoskeleton is made of chitin, a polysaccharide and, more specifically, a long-chain biopolymer of *N*-acetylglucosamine (see Figure 1).[22] The presence of −OH and $-NHCOCH_3$ polar groups in this polysaccharide is sufficient to chelate tin(II), and consequently, etching its surface is unnecessary.

Cicada exoskeletons appear on tree trunks and related structures during the months of July−September. They are also plentiful and free for the taking.[23] Beetles also have exoskeletons made of chitin.[24]

EXPERIMENTAL OVERVIEW: GENERAL CHEMISTRY AUDIENCE

Brass Washers

This experiment has been performed in one 3 h lab period by second-semester general chemistry students working in groups of four. Supporting Information Section S3 provides a detailed description of all the steps involved and includes questions answered by the students in their lab reports. Notes for the instructor are provided in Supporting Information Section S4. Answers to the questions posed to the students are supplied in Supporting Information Section S5.

Each group prepared 100.0 mL of the electroless nickel plating bath, which was first used to plate a ~0.75 in. diameter brass washer for 10 min and subsequently used to plate a pretreated cicada exoskeleton for 10 min. The electroless nickel plating bath was prepared from premade solutions from a commercial source (Caswell Inc.). The pH of the resulting nickel plating bath was ~5. The absorbance of the nickel

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Figure 2. Pretreated cicada exoskeleton being plated in the electroless nickel plating bath at 85 °C. Note the bubbles of $H_2(g)$ emanating from its surface.

Figure 3. Nickel-plated cicada exoskeleton being held by a neodymium magnet.

plating bath was measured at 394.7 nm to ensure the bath was properly prepared. The absorbance values hovered around 0.95 for the aforementioned solution.

Once the stirred nickel plating bath had reached 85 °C the brass washer was suspended in the bath and plated for 10 min. Plating was initiated by contact with a more active metal, specifically iron in the form of an iron nail. Once the plating process was initiated, bubbles of $H_2(g)$ were observed emanating from the surface of the washer, and $H_2(g)$ evolution continued throughout the entire plating process. The percent weight gain results for the brass washers fell in a range of 0.57 ± 0.20%. The appearance of the washer changed from its original golden brass color to a shiny silvery metallic color. The success rate of this process was 100%.

Cicada Exoskeletons

The cicada exoskeletons were cleaned in a degreaser bath prior to the start of the lab and rinsed several times with distilled water. Before the cicada exoskeletons were plated, they were subjected to a three-step pretreatment process. The steps were (1) immersion in an acidic tin(II) chloride solution for 5 min at 40 °C, (2) immersion in an acidic palladium(II) chloride solution for 5 min at 40 °C, and (3) immersion in a 3 M sulfuric acid solution for 4 min at 40 °C. After each step, the substrate was rinsed several times with distilled water.

In step 1 of the pretreatment protocol, Sn(II) cations were adsorbed (chelated) by the polar groups present in chitin. In step 2, the interaction between the chelated Sn(II) and Pd(II) ions resulted in a redox reaction where Sn(II) was oxidized to Sn(IV), and Pd(II) was reduced to Pd metal (see reaction 2).

$$Sn^{2+}(aq) + Pd^{2+}(aq) \rightarrow Sn^{4+}(aq) + Pd(s) \quad (2)$$

The end result of the redox reaction was the creation of Pd nanoparticles (or seeds) on the surface of the cicada exoskeleton. Step 3 was performed to remove residual tin salts from the surface of the exoskeleton.

After pretreatment, the cicada exoskeleton is plated in the electroless nickel bath held at 85 °C. Note the bubbles of $H_2(g)$ emanating from its surface (see Figure 2).

Like iron, nickel is ferromagnetic. If a thick enough coating of electroless nickel is deposited on the cicada exoskeleton, it can be picked up by a neodymium magnet (see Figure 3).

■ HAZARDS

Students performing the operations described above should wear goggles and gloves to prevent eye and skin contact with all chemicals. The plating and pretreatment procedures should be performed in a hood. All of the aqueous solutions should be disposed of in the hazardous waste containers supplied. The necessary precautions should be taken when working with the chemicals associated with the electroless nickel deposition: nickel(II) sulfate heptahydrate is a suspected cancer agent and toxic, sodium hypophosphite hydrate is hygroscopic, tin(II) chloride dihydrate is corrosive and toxic, palladium chloride is an irritant, hydrochloric acid is highly toxic and corrosive, and sulfuric acid is highly toxic and an oxidizer. The necessary precautions should also be taken when working with the

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chemicals associated with the electroless copper deposition: copper sulfate pentahydrate is toxic and an irritant; formaldehyde (37 wt % solution in water) is highly toxic and a suspected cancer agent; ammonium chloride is an irritant and hygroscopic; sodium hydroxide is corrosive and toxic; ethylenediaminetetraacetic acid is an irritant; glyoxylic acid monohydrate is corrosive and hygroscopic; citric acid causes severe eye irritation, and contact with skin should be avoided; and boric acid may damage fertility or an unborn child.

XRF RESULTS

Both the nickel-plated brass washers and nickel-plated cicada exoskeletons were examined by (energy-dispersive) X-ray fluorescence (XRF) spectrometry. The utility of this nondestructive analysis technique has been described in a number of articles in this *Journal*. Palmer has described the many advantages of XRF for elemental analysis as "minimal sample preparation, multielement analysis capabilities, detection limits in the low parts per million (ppm) range, and analysis times on the order of 1 min".[25] Substrates examined include geologic samples,[26] solid fossil fuel wastes,[27] early photographic processes,[28] and calcium in powdered milk,[29] among others. Our interest in XRF analysis of the nickel-coated substrates was to establish (1) that phosphorus was present in the nickel-plated coatings and (2) at what level phosphorus was present. These samples were analyzed "as is" using a hand-held XRF analyzer. Analysis time for each sample was 1 min. Additional information pertaining to the analyzer and a complete set of data are supplied in the Supporting Information (Section S6).

Table 4. XRF Results for Electroless Nickel-Plated Brass Washers

	Experimental Results (wt %)	
Constituent Elements	Average	Range
Phosphorus	3.95	2.48–5.42
Nickel	71.50	62.56–81.56
Copper	21.15	11.28–28.89
Zinc	1.37	0.00–5.42

The unplated brass washers were determined to contain 59.0% copper and 36.3% zinc. Five other metals were identified in the 0.5–1.5% range: K, Fe, Ni, Sn, and Pb. A dozen brass washers were examined by XRF after nickel electroless deposition for 40 min using a freshly prepared nickel bath (as described above) in each case. Table 4 summarizes the XRF results for the nickel-plated brass washers.

Only 4 out of the 12 Ni-plated washers had zinc values greater than 1%. The presence of 21% Cu in the nickel-plated washers suggests that the X-rays penetrated the nickel coating and also sampled the brass underneath the coating. However, there is a ~1.6:1 weight ratio of Cu to Zn present in the unplated brass washers that is absent in the nickel-plated brass washers. One possible explanation for the low Zn levels in the nickel-plated brass washers is that upon introduction of the washer in the plating bath (at 85 °C and a pH of ~5), the more active Zn is oxidized from the surface of the washer, whereas the less active Cu is not. Another possibility is that the Cu alloys with Ni because both adopt a face-centered cubic crystal structure, whereas Zn, which adopts a hexagonal close packed crystal structure, does not.

The cleaned cicada exoskeletons and nickel-plated cicada exoskeletons were also examined by XRF. For the cleaned but unplated cicada exoskeletons the following results were

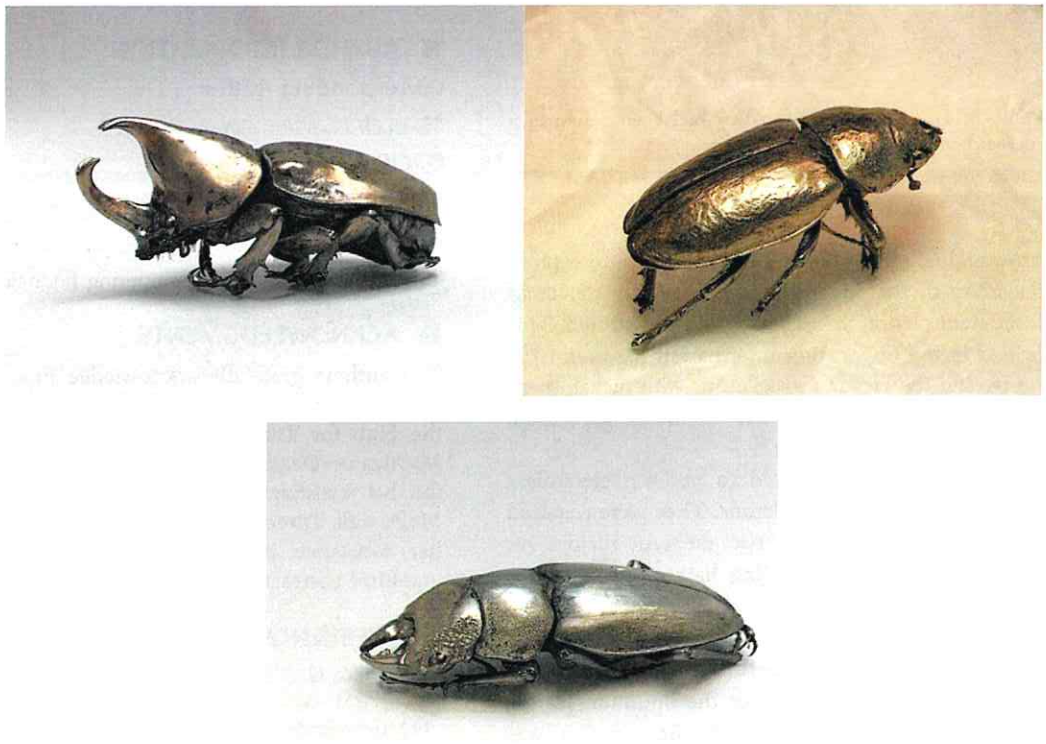

Figure 4. Photos of beetles that had been plated in an electroless nickel bath.

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obtained: P (average: 0.15%), Ni (not detected). After being plated for 10 min (as described above) the following results were obtained for five Ni-plated cicada exoskeletons: P (average: 7.21%, range: 5.40–8.88%) and Ni (average: 66.94%, range: 60.09–73.55%). Cicada exoskeletons that had been plated for longer time periods showed higher nickel and phosphorus values (e.g., Ni: 86.63 wt % and P: 11.73% after 1 h of plating).

The XRF measurements were obtained outside of the lab class, and the results were presented to the students. One of the questions the students were asked to answer in their lab report pertained to the XRF results. They were asked to summarize the results, draw conclusions about the nature of the nickel coatings, and explain any anomalies connected with the results.

EXPERIMENTAL OVERVIEW: UPPERCLASS CHEMISTRY MAJORS

These students worked on three projects. They plated brass washers employing the same nickel plating bath and the same protocols as described above. Their assignment was to explore the reproducibility of the weight gain incurred by the brass washers for different plating times: 10, 20, 30, and 40 min. This data is provided in the Supporting Information (Section S7).

Figure 5. Photo of a cicada exoskeleton that had been plated in a copper electroless bath.

Instead of plating the cicada exoskeletons with nickel, these students plated dead beetles which were found or purchased. Some results are pictured in Figure 4.

The students were also challenged to perform electroless copper deposition on cicada exoskeletons. They were required to do a literature search and find two different recipes for preparing an electroless copper plating bath along with the plating parameters. After consultation with the instructor, the students were supplied the necessary chemicals and performed the electroless copper plating process on the cicada exoskeleton. Their goal was to discover the optimum plating temperature and to demonstrate that the process was reproducible. A copper-plated cicada exoskeleton is pictured in Figure 5. Further details including references, recipes, and outcomes are supplied in the Supporting Information (Section S4).

CONCLUSIONS

This laboratory experiment showcases an important industrial process: electroless deposition. It also expands the students' appreciation of the many facets of applied electrochemistry. General chemistry students have successfully performed this lab experiment in one lab period on several occasions. They rate this experiment as one of their favorites and are fascinated that the cicada exoskeleton is readily plated with nickel. An extensive set of questions that are answered as part of the lab report allows the instructor to (1) revisit past topics (e.g., acid–base chemistry, buffers, electronic spectra, and Beer's Law), (2) explore the redox chemistry connected with the experiment (e.g., calculation of E^0_{cell} for the Sn^{2+}/Pd^{2+} reaction and why Ni^{2+} cannot be substituted for Pd^{2+}), (3) explore new topics (e.g., the composition of brass versus that of bronze, determination of the thickness of the nickel coating on the plated brass washer, and the XRF results for the brass washers and cicada exoskeletons), and (4) explore reasons for the variation in weight gain observed for the brass washers. These questions are located in Supporting Information Section S3, and the answers to the questions are included in Supporting Information Section S5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00055.

Proposed mechanisms for electroless nickel deposition and electroless copper deposition, lab instructions for students and instructor, notes for the instructor, answers to lab questions, XRF results, and weight gain data for the brass washers (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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